

Quasicrystals: A New State of Matter?

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The identification of the occurrence of a material which has a structure that is ordered but not periodic in an electron diffraction work triggered a sensational discovery in 1984. It was found that a rapidly solidified alloy of Al with 10–14% Mn possesses an icosahedral symmetry in combination with long-range order. The discovery of such aperiodic forms has resulted in rewriting the basics of crystallography and has paved the way to search for these materials in Nature and look for specific applications.

For a long time it was me against the world. I was a subject of ridicule and lectures about the basics of crystallography. The leader of the opposition to my findings was the two-time Nobel Laureate Linus Pauling, the idol of the American Chemical Society and one of the most famous scientists in the world. For years, 'til his last day, he fought against quasi-periodicity in crystals. He was wrong, and after a while, I enjoyed every moment of this scientific battle, knowing that he was wrong.

Dan Shechtman

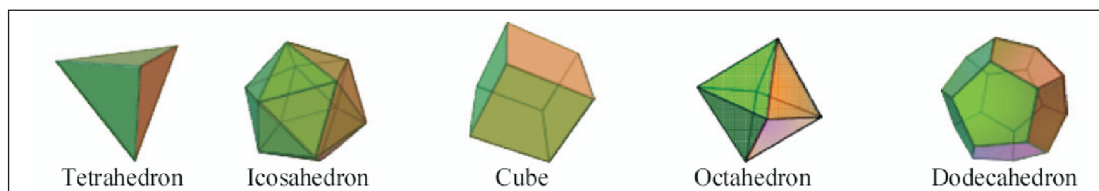
‘Controversial yet brilliant’ is the best way to describe the work on quasicrystals which earned Dan Shechtman the Nobel Prize in Chemistry in 2011. In fact the Nobel Committee at the Royal Swedish Academy of Sciences said that “his discovery was extremely controversial,” but that his work “eventually forced scientists to reconsider their conception of the very nature of matter.”

It all started with the Hindu Samkhya Philosophy which identifies the five basic elements as the ‘Pancha Mahabuthas’; *Prithvi* or *Bhumi* (Earth), *Áap* or *Jala* (Water), *Agni* or *Tejas* (Fire), *Vayu* or *Pavan* (Air or Wind), and *Akasha* (Aether). Indeed, the

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philosophical note of Plato (428–328 BC) identified the elements of Nature (fire, air, earth, water and the universe) with regular solids, the five platonic solids (*Figure 1*). *Tetrahedron* having the smallest volume for its surface area was identified with *fire* whereas *icosahedron* with its largest volume was identified with *water*. Plato also identified the *cube*, standing firmly on its base, to correspond to the stable *earth*; and *octahedron*, which can rotate freely when held by two opposite vertices to correspond to the mobile *air*. The *dodecahedron* with its twelve faces was identified to represent the *universe* keeping in view that the zodiac has 12 signs. In principle, these regular solids should represent three-dimensional objects of Nature and hence all crystalline materials should have these as basic building blocks. However, crystalline materials are also associated with translational periodicity and the basic repeat units should be close packed. These requirements generate the seven crystal systems, 32 point groups and 230 space groups for a complete description of 3D objects.

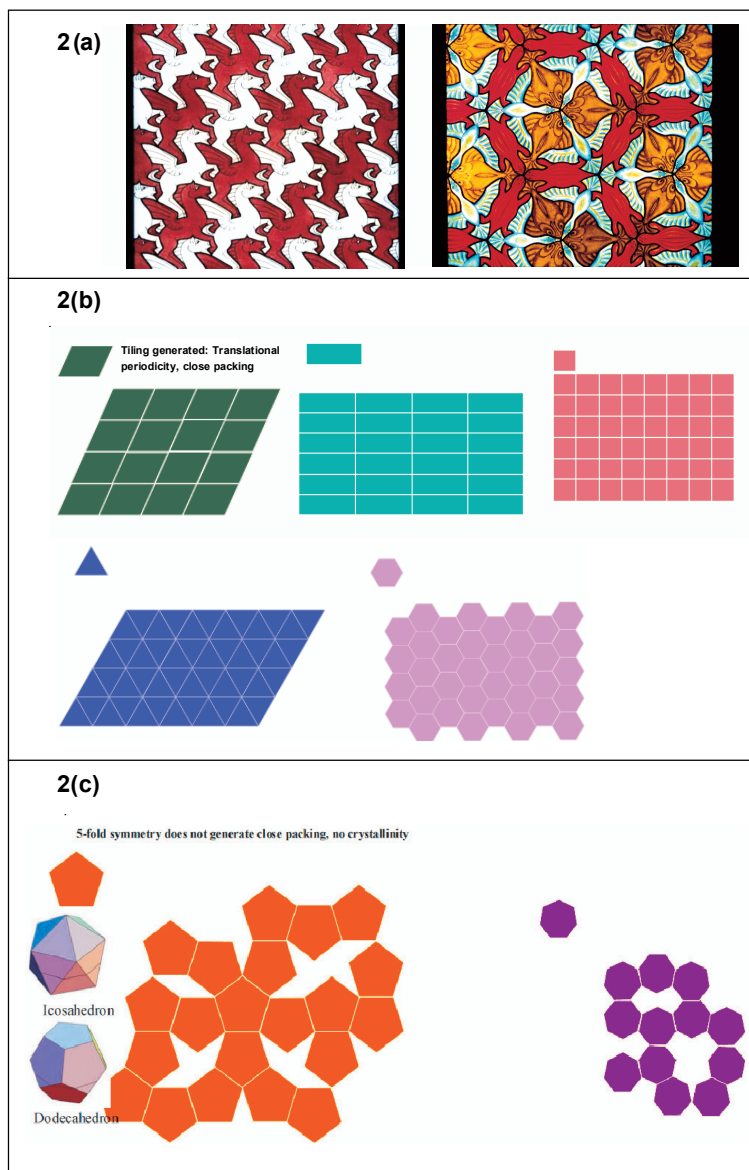
The presence of translation periodicity in the 2D lattice generated by closely packed objects as shown in *Figure 2* produces a tiling automatically associated with a rotational symmetry. The basic rules of crystallography allows only 2, 3, 4 and 6 rotational symmetry to generate close-packed structures which in turn will produce diffraction spots corresponding to the symmetry in these objects when exposed to X-radiation. *Figure 2c* demonstrates that close packing cannot be achieved with 5-fold and 7-fold symmetry and hence it is practically impossible to form crystalline objects with this rotational symmetry. In case of 3D objects it is possible to obtain an infinitely extended crystal structure by aligning building blocks called ‘unit-cells’ to entirely fill the three-dimensional space. These crystal structures are restricted

Figure 1. Regular (platonic) solids; will they give a three-dimensional lattice with periodicity?

Two of the regular solids, icosahedron and dodecahedron possess 5-fold symmetry and as a consequence X-ray diffraction patterns of crystalline materials will not display such symmetry.



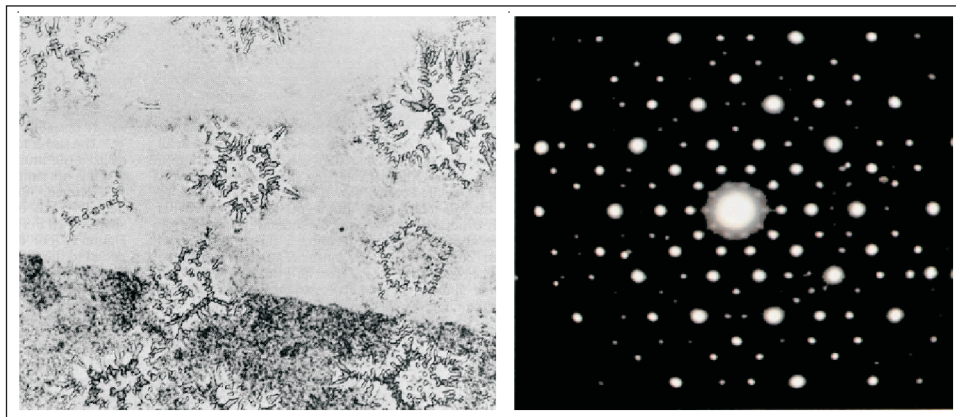
Figure 2. (a) M C Escher's drawings depicting translation and rotation + translation symmetry. (b) The five allowed planar lattices with close packing to generate infinite lattices (tiling). (c) 5-fold and 7-fold plane lattices cannot generate close packing; however two of the regular solids, icosahedron and the dodecahedron display 5-fold symmetry, and this is an enigma.



by the requirement of close packing involving the rotational and translational symmetry elements, and diffraction patterns of these normal crystals belong to one of the 11 Laue-groups. However, two of the regular solids, icosahedron and dodecahedron possess 5-fold symmetry and as a consequence X-ray diffraction patterns of crystalline materials will not display such symmetry.

In 1984, Shechtman, Blech, Gratias and Cahn [1] showed that the





electron diffraction patterns of a rapidly solidified alloy of Al with 10–14% Mn possesses icosahedral symmetry in combination with long-range order. The sharp reflections display a clear 10-fold symmetry in reciprocal space contrary to crystallographically accepted norms (*Figure 3a–c*). These observations initially confused the authors; however they were able to explain the spectacular diffraction patterns by invoking the 5-fold symmetry as shown in *Figure 3c*.

At the outset, these observations resulted in a sensational discovery of disallowed symmetry in crystalline materials (based on sharp diffraction data) and demanded a satisfactory explanation. The crystals then would possess a ‘Quasi-Periodicity’, representing a new class of materials and crystallographic rules need to be revisited. Interestingly, earlier mathematical predictions starting from the surmise of 1D quasi-periodicity in a Fibonacci chain suggest such a deviation from ideality. A simple example of the Fibonacci sequence is as follows: 1, 1, 2, 3, 5, 8, 13 Each term in this sequence is simply the sum of the two preceding terms; however a more interesting observation is the quotient of the adjacent terms that possesses an amazing proportion, roughly 1.618, or its inverse 0.618. This proportion is known by many names: the golden ratio, the golden mean, PHI (φ) and the divine proportion. Interestingly, almost everything which has dimensional properties that adhere to the ratio of 1.618, seems to serve as a fundamental function for the building blocks in Nature.

Figure 3a. Electron micrograph and the corresponding diffraction pattern showing 10-fold symmetry.

Courtesy: P J Steinhardt

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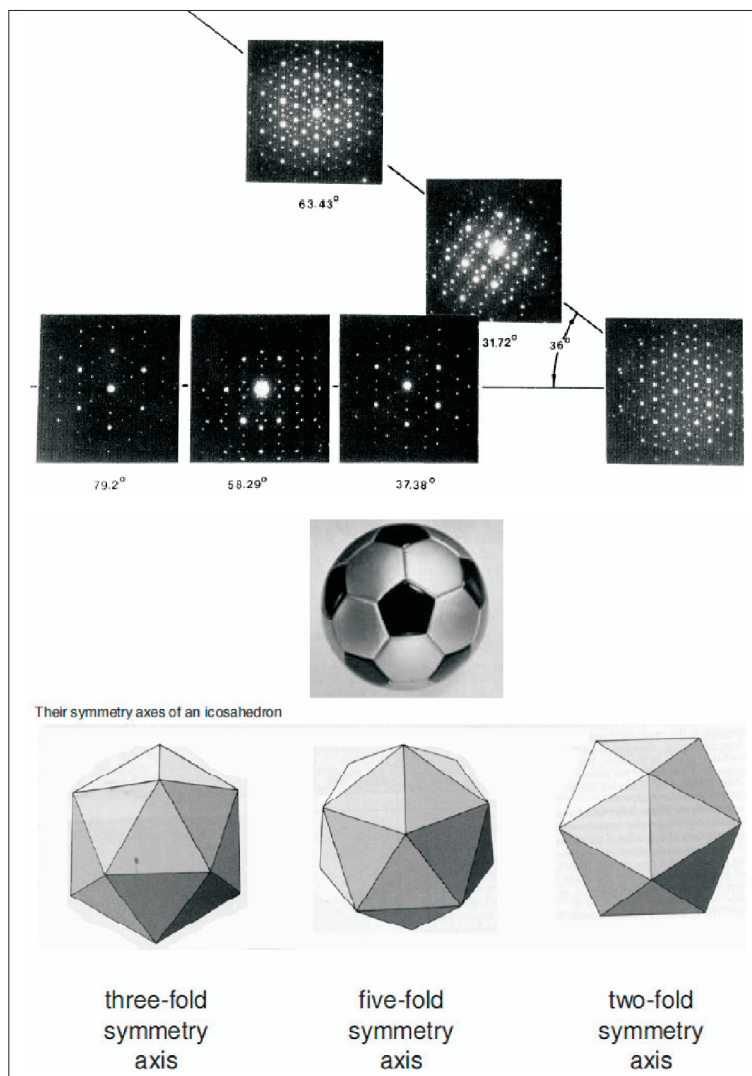
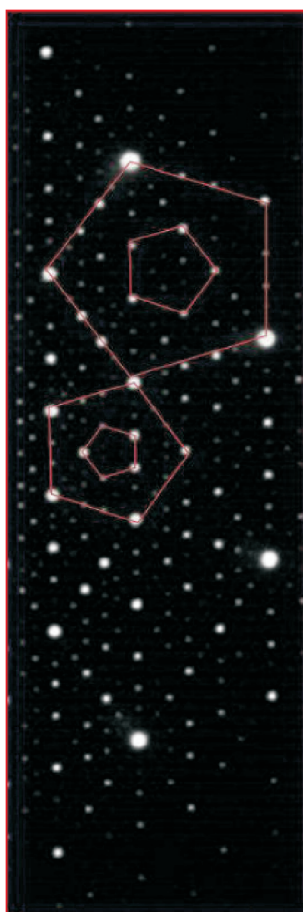


Figure 3b. The icosahedral symmetry (football) indicating the presence of 3-, 5-, 2-fold axes and the sections of the diffraction pattern supporting the presence of icosahedral symmetry (a forbidden symmetry!).

Courtesy: P J Steinhardt

Figure 3c. Portion of the electron diffraction pattern highlighting the forbidden pentagon traces of the diffraction pattern.

Courtesy: P J Steinhardt



Indeed the perfect pentagons shown in *Figure 3c* linearly scale to

$$\varphi = \frac{1 + \sqrt{5}}{2} = 1.6180339887\dots$$

Hence, the pattern recorded from the electron diffraction must be periodic, or more appropriately quasi-periodic which thus explains the occurrence of well-defined diffraction pattern with disallowed symmetry! The description hence becomes a bit more complex and rules of crystallography in 3D space should now be expanded to higher dimensional space.



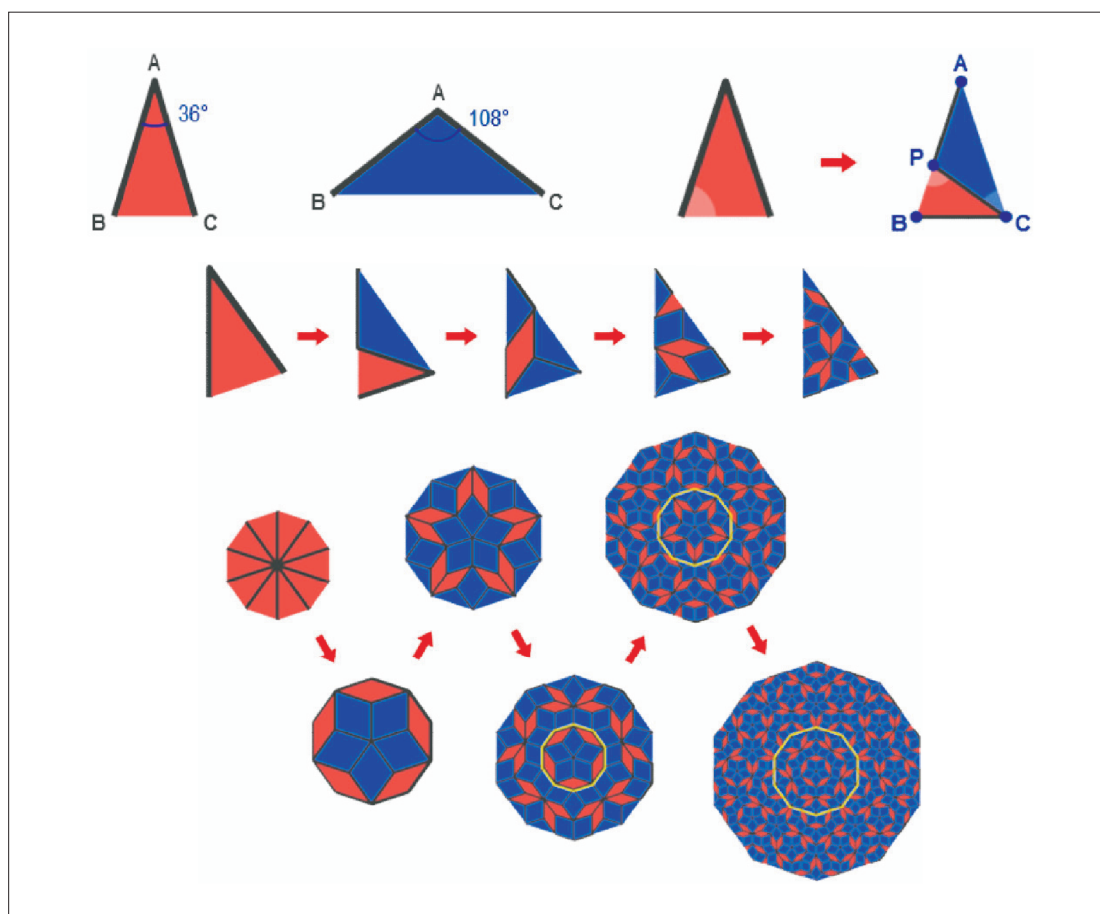
Roger Penrose [2] introduced the concept of non-periodic tiling which implies that a shifted copy of this tiling will never match the original. This tiling has remarkable properties: for example (1) it is non-periodic, lacking any translational symmetry, and (2) it is self-similar, so the same patterns can occur at larger and larger scales and any finite patch from the tiling can occur many times extending to infinity resulting ultimately in a lattice. The following methodology explains the concept of tiling and the eventual generation of infinite lattices.

Two triangles (red and blue) have internal angles of 36° and 108° respectively (see *Figure 4*). The red triangle can be subdivided with the generation of the vertex P which divides AB following the golden ratio. Continuing the subdivision, the basic repeat unit

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Figure 4. Demonstration of generation of quasi-infinite Penrose tiling with long-range order.

Courtesy: Python website

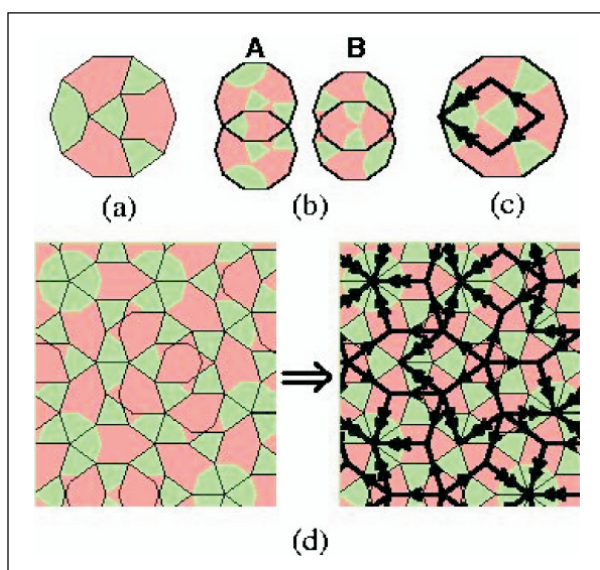


Gummelt showed that Penrose tilings can be generated by a single aperiodic 'prototile'.

can be generated which does eventually produce close packing but not involving any of the accepted 2, 3, 4 and 6 rotational symmetry elements. The final illustration in *Figure 4* represents a close-packed two-dimensional lattice with a ten-fold symmetry (resembles the diffraction pattern obtained in *Figure 3a*). However, this feature requires two clusters corresponding to obtuse and acute rhombic tiles without matching rules. As more and more quasicrystalline materials were discovered, the identification of two clusters satisfying the density ratios for the formation of Penrose tiling became superfluous [3]. Further, quasicrystals are essentially made of metals with no covalent bonding among clusters, finding energies to activate the matching rules become highly restrained. Gummelt [4] showed that Penrose tilings can be generated by a single aperiodic 'prototile'. However, instead of edge-to-edge matching rules, the copies of the 'prototile' may intersect in sets with nonempty interior as shown in *Figure 5* to form a decagon. Steinhardt and H-C Jeong [5] proposed a single cluster model based on simple thermodynamic considerations. The single repeating cluster is akin to the unit cell in a periodic crystal and has the propensity to overlap with the neighboring clusters with sharing of the atoms in the common areas of the two clusters resulting in the interpenetration of the clusters.

Figure 5. A quasiperiodic tiling can be forced using marked decagons shown in (a). Matching rules demand that two decagons may overlap only if shaded regions overlap. This permits two possibilities in which the overlapped area is either small (A-type) or large (B-type), as shown in (b). If each decagon is inscribed with a large obtuse rhombus, as shown in (c), a tiling of overlapping decagons (d, left) is equivalent to a Penrose tiling (d, right).

Courtesy: P J Steinhardt



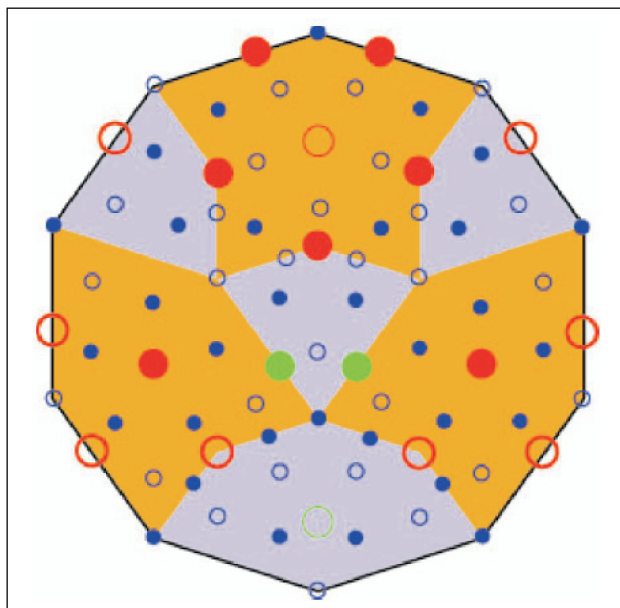


Figure 6. A candidate model for the atomic decoration of the decagonal quasi-unit cell for $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$. Large circles represent Ni (red) or Co (purple) and small circles represent Al. The structure has two distinct layers along the periodic c -axis. Solid circles represent $c = 0$ and open circles represent $c = 1/2$.

Courtesy: P J Steinhardt

This paved the way for solving the crystal structures of quasicrystals by a simple decoration of the clusters as shown in *Figure 6*. The quasi-unit cell picture has been applied to the study of the structure of the decagonal phase of $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ [4], one of the best-characterized quasicrystalline materials and an excellent candidate for comparing structural models of quasicrystals. The quasi-unit cell picture replaces the Penrose tiling picture as a model for the ideal quasicrystal structure. According to the quasi-unit cell picture, the structure is determined entirely by a single repeating cluster which overlaps (shares atoms with) neighbor clusters according to simple energetics. One unique feature in the structure is that the atoms can be associated with the cluster and the single repeating cluster (which is the unit cell equivalent) but can share atoms (*Figure 6*) with neighboring clusters. It is of interest to note that the atomic decoration of the quasi-unit cell also encodes the symmetry of the structure. It is exciting to realize that the determination of the structure of quasicrystals thus is simply a decoration of the overlapping units of the identified cluster with shared atoms which overlaps with the neighboring clusters to produce the required quasicrystalline features. The non-involvement of complicated structure determination

The quasi-unit cell picture replaces the Penrose tiling picture as a model for the ideal quasicrystal structure.



Dov Levine and Paul Steinhardt, in addition to their valuable theoretical contributions, coined the name “quasicrystals”.

protocols like Direct Methods or Patterson Approaches for solving regular crystal structures is indeed an unexpected reward!

As with any area in science there are several other rich and major contributions to the discovery of quasicrystals. Dov Levine and Paul Steinhardt [6], in addition to their valuable theoretical contributions, coined the name “quasicrystals”. Alan Mackay [3] recognized the significance of the diffraction by simulating the pattern for the then hypothetical three-dimensional Penrose pattern (ordered but not periodic). There were some significant contributions from India to this area, in fact K Chattopadhyay and S Ranganathan discovered decagonal quasicrystals in 1985 [7], and P Ramachandra Rao and G V S Sastry produced a new type of quasicrystal in Mg–Al–Zn alloy also in 1985 [8].

Indeed, quasicrystals have always been synthetic intermetallics, and in recent times hundreds of intermetallic systems have been shown to yield quasicrystals. However quasicrystalline features are hardly seen in other types of materials. Dendrimer liquid crystals [9], star copolymers [10] and recently self-assemblies of nanoparticles [11], have shown quasicrystalline nature. Several alloys have been found since then in various laboratories around the world; however the quest to discover naturally occurring quasicrystals met with success recently in 2009. The naturally occurring quasicrystalline mineral icosahedrite has been identified in a sample from the Khatyrka River in Chukhotka, Russia [12,13] (see *Figure 7*).

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In a nutshell, quasicrystals like normal crystals display (1) orderly arrangement, but *quasi-periodic* instead of *periodic*, (2) rotational symmetry, but with *forbidden* symmetry and (3) structure that can be reduced to a finite number of repeating units and the structure determination is facile as it just involves the decoration of atoms to associate with the repeat cluster (the unit cell in quasicrystals).

Well, then why a Nobel Prize for this discovery in laboratory-made materials? The Nobel Committee writes in the citation “ In



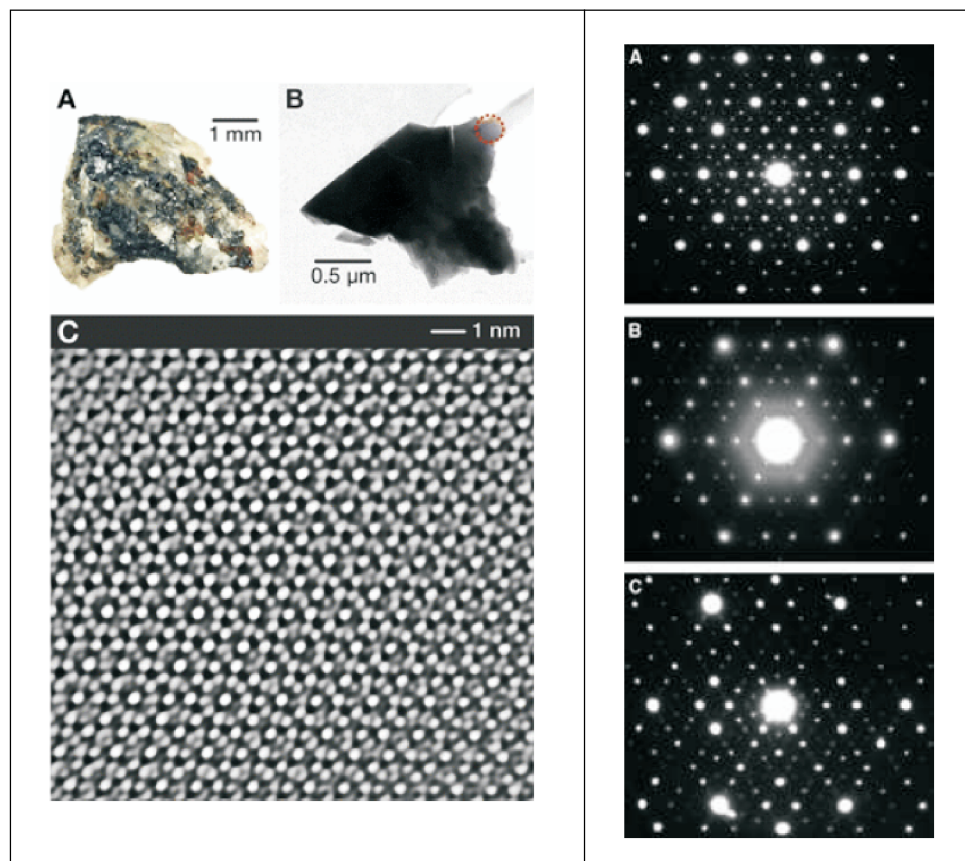


Figure 7. (Left) (A) The original khatyrkite-bearing sample used in the study. The lighter-colored material on the exterior contains a mixture of spinel, augite, and olivine. The dark material consists predominantly of khatyrkite (CuAl_2) and cupalite (CuAl) but also includes granules, like the one in **(B)**, with composition $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$. The diffraction patterns were obtained from the thin region of this granule indicated by the red dashed circle, an area $0.1 \mu\text{m}$ across. **(C)** The inverted Fourier transform of the HRTEM image taken from a subregion about 15 nm across displays a homogeneous, quasi-periodically ordered, five-fold symmetric, real space pattern characteristic of quasi-crystals.

(Right) Diffraction patterns obtained from natural quasi-crystal grain.

Courtesy: P J Steinhardt

quasicrystals, we find the fascinating mosaics of the Arabic world reproduced at the level of atoms: regular patterns that never repeat themselves. However, the configuration found in quasicrystals was considered impossible, and Dan Shechtman had to fight a fierce battle against established science. The Nobel Prize in Chemistry 2011 has fundamentally altered how chemists conceive of solid matter.”

The Nobel Prize in Chemistry 2011 for Dan Shechtman has fundamentally altered how chemists conceive of solid matter.



Acknowledgement

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